

INVESTIGATION OF THE CO₂ ABSORPTION CAPACITY OF DRY FGD WASTES

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ABSTRACT

Numerous utility boilers and tail-gas desulfurization units utilize lime or limestone-based sorbents to remove sulfur oxides generated during the combustion of fossil fuels. Such units generate about 20 million tons of flue-gas desulfurization (FGD) wastes annually in the U.S., the bulk of which (~95%) is discarded in landfills or holding ponds.¹ Thus, commercial utilization of FGD wastes would benefit from both a plentiful low-cost raw material as well as a significant savings in disposal. One such use may be for the reduction of CO₂ in multi-component gas streams.

During the removal of SO₂, the lime added to or generated in the desulfurization unit, is not fully utilized. That is, a portion of the Ca fed to the unit is not sulfated (remains as CaO or Ca(OH)₂). In some FGD wastes, the fraction of available Ca is quite high (> 1/3), particularly for dry wastes. When hydrated, such wastes exhibit a strong affinity to absorb CO₂ at ambient temperature. Further, both the kinetics and extent of absorption are favorable as CO₂ initially at ~2.5 volume% was rapidly reduced to below the detection limit of the measurement device (ppm range) used in this study. Leaching behavior and changes in the mineralogy of the FGD samples exposed to CO₂ are also discussed.

INTRODUCTION.

Over the past decade, numerous FGD units have been added to existing utility boilers in an effort to satisfy federal mandates on SO₂ emissions. Such units are usually classified as either wet or dry depending on whether the absorbent is used in a slurry (wet) or as a hydrated solid. Wet scrubbers capture sulfur chiefly as gypsum (CaSO₄·H₂O) with some sulfite formation (e.g., CaSO₃·2H₂O). Dry technologies such as AFBC produce a dry product in which sulfur is captured mostly as anhydrite-CaSO₄ or for the dry tail-gas units such as spray drier and duct-injection, sulfur is captured as gypsum, anhydrite or hemi-hydrate (CaSO₄·H₂O). Dry FGD by-products also differ from their wet-scrubber counterparts in that a significant portion of the calcium in the dry waste remains unsulfated. This Ca is present as either calcium oxide, CaO, or as slaked lime, Ca(OH)₂. Because FGD wastes, particularly dry FGD wastes represent relatively new materials, <6% of the ~20 M tons of FGD wastes generated in 1993 are currently finding commercial uses.¹

The work described here represents a preliminary examination of the capacity of dry-FGD wastes to remove CO₂ from multi-component gas streams. Such an absorbent may have numerous commercial uses, e.g., gas purification, removal of CO₂ during H₂ production, etc. However, the current study focused on the potential to reduce CO₂ in simulated natural-gas streams. As a rule of thumb, the costs associated with available CO₂-removal technologies (wet scrubbers, molecular sieves, membranes) are prohibitive for gas wells that produce less than about 100,000 SCF/day.² This effectively eliminates commercial production from low-porosity, carbonate-containing strata common to many gas-producing deposits. Thus, a low-cost CO₂ absorbent that can be safely disposed or marketed (road base or fertilizer) may have applications in the natural-gas industry.

In this study, CO₂ absorption capacity was evaluated for waste samples generated from different utility boilers, one demonstration plant, and tests conducted under four sets of conditions in a single pilot plant. With the exception of a utility-derived fly ash used as a control, all samples examined are dry-FGD waste materials. Absorption capacity was examined for both hydrated samples as well as aqueous slurries. As of this writing, only gas blends containing inert gases and CO₂ or inert gas and CO₂/CH₄ have been tested. Additional tests are planned to evaluate absorption behavior during exposure of hydrated FGD-wastes to a gas blend containing H₂S, CO₂, and CH₄.

EXPERIMENTAL.

Absorption Reactor. A schematic of one configuration of the reactor used to measure CO₂ absorption for the hydrated samples is shown in Figure 1 (shown with 9" X 1/4"-i.d. tube reactors). This is essentially the reactor described in earlier adsorption/cracking studies of liquid hydrocarbons³ with some modification. The more significant modifications include the introduction of standard gases containing CO₂/Ar or CO₂/CH₄/Ar via the entry line in which pure Ar was previously metered, plugging of the liquids inlet, use of 4" X 3/8"-i.d. reactors in addition to the 9" X 1/4" reactors (most of the hydrated-sample tests), and placement of the 4" reactors in a vertical alignment to provide a more uniform flow of gases through the hydrated samples. Essentially the same measurement system was used to measure absorption of CO₂ by the water/sample slurries except that a pair of 250-mL-capacity gas scrubbers were substituted for the ss tube reactors.

Samples. Many of the study samples examined were obtained from commercial utilities that

preferred to remain unidentified. Thus, only cursory descriptions of the samples will be given and some producers will remain anonymous.

A total of 11 samples were examined. A very brief description along with the identification label used in this report is given in Table I. The fly ash utilized as control (L-FA) is a Class F fly ash from a pulverized-coal-combustion (PCC) utility boiler operating on bituminous coal. The fluidized-bed combustion materials (FU-FA/BA and CC-FA/BA) were derived from circulating or entrained flow units operating on high-sulfur bituminous coal. The coarse material (BA-bed ash) was drained from the bed while the finer material (FA) represents cyclone and baghouse catch. These samples differ primarily in particle size and relative proportions of free lime. Two types of dry post-combustion flue-gas material were utilized in the study, a spray-dryer ash from a large industrial boiler in the Midwest, and materials from the Coolside duct-injection technology. The Coolside materials include a sample (CS) from Ohio Edison's 1990 demonstration of the technology at its Edgewater power plant⁴ as well as materials derived from the CONSOL's Coolside pilot plant in Library, PA (PP1-PP4).⁵

Run Conditions and Procedures. All absorption measurements were made at ambient temperature. Nominal gas flows of 100 mL/min (ambient temperature) for the hydrated-solids tests and 150 mL/min for the slurry tests were metered through each reactor. The gas streams were comprised solely of N₂ in the bypass line and a standard-gas blend (either Ar/CO₂/He-7.5/2.5/90.0 vol%; or Ar/CO₂/CH₄-30.4/49.6/20.1 vol%) in the absorbent line. Argon was included as a tracer gas to eliminate measurements problems associated with minor leaks or instrumental drift.

Hydrated samples of known water content were obtained by careful blending of distilled water and dry waste. Between 2 and 5 g of the hydrated samples were packed into the absorbent reactor between quartz-wool plugs. The bypass reactor was packed with 6 g of Ottawa sand.

For the slurry absorption experiments, ~5 g of dry sample was added to 200 mL of distilled water in a 250-mL gas scrubber. The slurry was stirred with a magnetic stir bar for the duration of the experiment. Gas concentrations in the combined sample/bypass exit stream were determined with a VG-quadrupole mass spectrometer (QMS). This unit was operated in a selected-ion-monitoring mode in which intensities for m/e 18-H₂O⁺, 20-Ar²⁺, 28-N₂⁺, 40-Ar⁺, 44-CO₂⁺, and 15-CH₃⁺ (for methane) were recorded at approximately 1-second intervals.

For both the hydrated-solids and slurry tests, data collection was initiated with the switching valve in the bypass position, i.e., with the CO₂ stream passing through the bypass reactor. After a minimum of 150 data points were collected (usually 2-4 minutes), the valve was rotated so that the CO₂ stream was switched to the absorbent reactor and the N₂ stream was simultaneously switched to the bypass reactor. After a selected exposure time, the valve was returned to the initial position to reestablish the QMS baseline.

Following data collection, the QMS data were imported to a spreadsheet where the molecular-ion signal for CO₂ (m/e-44) was ratioed to the Ar-ion signal (m/e-40). The curves described by the CO₂/Ar ratio were then numerically integrated over the interval during which CO₂ was routed to the absorbent reactor to determine the fraction of the CO₂ absorbed. The fraction of CO₂ absorbed was calculated to an absolute basis then to SCF of CO₂ absorbed per ton of waste.

Several of the hydrated samples were retained in sealed vials for post-run XRD analysis to investigate changes in mineralogy resulting from CO₂ absorption. Likewise, selected slurry waters were retained in sealed containers for ICP analysis of heavy metals/cations.

RESULTS

A plot of the CO₂/Ar ion-intensity ratios is shown in Figure 2. In this run, the Ar/CO₂ blend (2.5% CO₂) was initially flowed through the sand-packed bypass reactor, switched to the absorbent bed packed with hydrated FU-fly ash at 3 min, returned to the bypass reactor at 53 min, then again to the absorbent reactor 3-min later. This particular plot demonstrates both the rapid kinetics and the extent to which CO₂ was absorbed in the 9" reactor as well as provides an indication of the reproducibility of the QMS response during the two bypass- and expose-mode intervals. A more complete run, also conducted in the 9" reactor with 2.5% CO₂, is shown in Figure 3. This latter plot demonstrates how the QMS response collected as the CO₂ passes through the bypass reactor (before and after the valve switch) provides a suitable baseline for integration of the ion intensities recorded during passage of CO₂ through the absorbent bed.

Absorption by hydrated solids. Absorption of CO₂ is shown in Figure 4 as a function of water content. These plots were prepared from runs in which 2-5 g (dry basis) of hydrated sample were exposed to flowing CO₂ (49.6%; ~100 mL/min) in the 4" X 3/8"-i.d. reactors. In dry form, none of the wastes examined showed a strong affinity for CO₂. However, with addition of H₂O, the absorption capacity increased rapidly until the water content was sufficiently high to create a mud-like texture in the waste samples. At the highest moisture levels, absorption capacities declined, presumably limited by sample permeability. Maximum absorption ranged from ~1,700 SCF/ton for the FU-FA to ~300 SCF/ton for the control fly-ash sample (L-FA). Limited testing in the 9" reactor showed absorption in excess of 2,000 SCF/ton for the FU-FA sample.

Absorption by water/waste slurries. For the final phase of the study, the ss tube reactors were replaced with a pair of 250-mL gas bubbler/scrubbers. As described earlier, ~5 g of solid waste were added to 200 mL of distilled water in the absorbent scrubber (bypass scrubber contained 200 mL of distilled water). The gas blend containing CO₂, Ar, and CH₄ (~50:30:20) was bubbled through the water in the bypass reactor during the initial bypass interval then switched to the absorbent slurry for up to one hour before returning to bypass. The QMS data collected during the slurry tests was processed the same as those collected during the hydration studies.

Results from the slurry tests are shown in Figure 5. Absorption ranged from less than 1,000 SCF/ton for the L-FA control sample to more than 3,500 SCF/ton for the FU-FA and PP4 samples. These results generally correlate with the free lime data in Table I with the exception of the two samples of bed ash. The significantly larger particle size of the bed ash samples likely limits diffusion of CO₂ into the particle and explains their lower than expected absorption capacity.

Although removal of CO₂ was greater in the slurry tests on an absolute basis, neither the rate or level of maximum absorption was as great as measured for the equivalent hydrated samples. Slurry runs typically required 10-20 minutes before CO₂ response returned to 95% of the original level. Further, at maximum absorption, CO₂ was typically reduced from 49.6% in the feed stream to around 12-15% in the exit stream for the slurry tests as compared to 1% or less in the exit stream for the hydrated-waste tests. However, the shape of the adsorption curves obtained from the slurry tests is thought to be more of a reflection of scrubber design rather than absorption kinetics. It is believed that both kinetics and the maximum level of absorption can be markedly improved with a more efficiently designed bubbler/scrubber (smaller bubbles, longer contact time).

Post-run analysis of hydrated solids and slurry waters. Selected samples from the hydration tests were examined by XRD and compared to similar analyses of unexposed samples. The XRD results indicate that the only significant change in mineralogy following absorption was an increase in calcium carbonate (CaCO₃). There was also a minor increase in ettringite, a hydrous calcium sulfaluminate phase that can substitute carbonate for sulfate in its structure. However, since the samples remained moisturized following exposure (i.e., they may continue to react), it is possible that these minor changes occurred after the absorption run and before the XRD analysis. Regardless, it appears that the CO₂ reacts primarily with available Ca (CaO or Ca(OH)₂) to form carbonate.

Two of the water samples retained from the slurry tests were analyzed for metal/cations content (Table II). Elemental concentrations are in large part controlled by pH which was >12 for these samples. At such high pH, most transition metals are relatively insoluble. This likely explains why none of the elements tested were detected at levels sufficient to suggest unreasonable disposal problems due to the leaching of toxic elements from the waste samples into the slurry water.

SUMMARY

The results obtained in this study clearly show that when hydrated, FGD wastes exhibit a high affinity for CO₂, ranging as high as 3,600 SCF/ton. Further, there are significant differences in the capacity of FGD wastes generated in different plants to absorb CO₂. With the exception of the larger particle-size bed-ash samples, these differences appear to be controlled by the available lime content of a given waste. This is supported by the free-lime data in Table I and XRD analysis which indicated that the absorbed CO₂ reacts with free lime to form CaCO₃. Thus, dry wastes from less efficient utility scrubbers should produce higher-capacity CO₂ absorbents. Finally, analysis of the slurry waters suggests that process waters that may be used in a liquid scrubber can be safely disposed following contact with FGD wastes.

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Table I. Waste samples examined.

Sample#	Label	FGD Waste	Free CaO (wt%)	Source/Comment
1	L-FA	N	2.7	Utility-boiler fly ash
2	FU-FA	Y	19.5	Fluidized bed-cyclone/baghouse catch
3	FU-BA	Y	26.8	Fluidized bed-bed ash
4	SD	Y	5.8	Utility spray dryer
5	CC-FA	Y	8.6	Fluidized bed-cyclone/baghouse catch
6	CC-BA	Y	21.2	Fluidized bed-bed ash
7	PP1	Y	12.9	Coolside pilot plant waste
8	PP2	Y	9.1	Coolside pilot plant waste
9	PP3	Y	8.5	Coolside pilot plant waste
10	PP4	Y	19.9	Coolside pilot plant waste
11	CS	Y	6.5	Coolside demonstration plant waste

Table II. Concentration (ppm) of cation/metals in the waters retained from slurry-absorption tests.

	FU-FA	FU-BA		FU-FA	FU-BA
Ag	<.01	<.01	Mg	87	34
Al	<.05	<.05	Mn	0.013	0.080
As	<.03	<.03	Mo	0.085	0.075
B	5.7	3.9	Na	3.85	0.85
Ba	0.020	0.010	Ni	<.005	0.017
Ca	558	565	P	<.05	<.05
Cd	0.001	0.001	Pb	<.01	<.01
Co	<.005	<.005	Se	<.03	<.03
Cr	<.005	<.005	Si	23	42
Cu	<.005	<.005	Ti	0.013	0.013
Fe	0.015	0.013	V	0.071	0.038
K	3.50	0.45	Zn	0.012	<.002

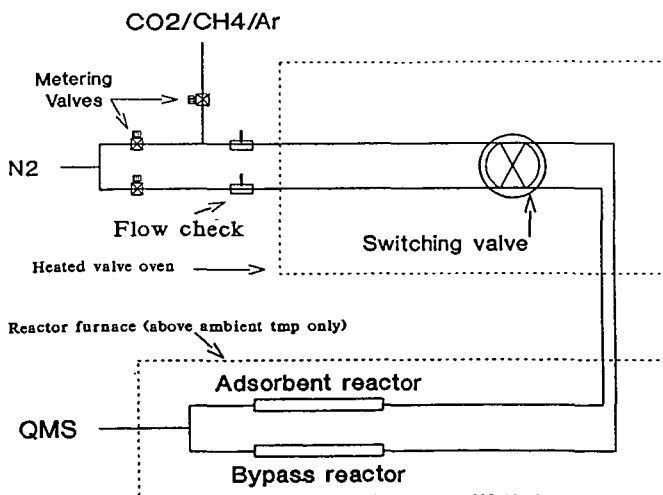


Figure 1. Schematic of the absorption reactor used for the hydrated samples.

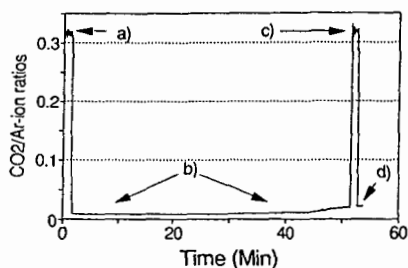


Figure 2. CO₂/Ar ion-ratio curve showing CO₂/Ar ratios as gas blend is routed through a) bypass reactor, b) absorbent reactor, c) return to bypass reactor, and d) return to absorbent reactor.

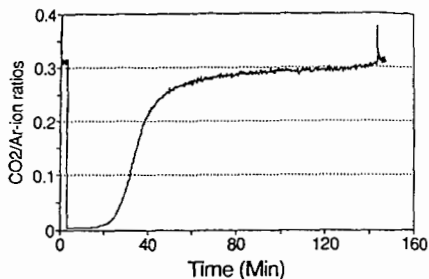


Figure 3. CO₂/Ar ion-ratios during run with FU-fly ash in 9" reactors (1.5 g dry FU-FA; 0.58 g H₂O; 2.5 mL/min CO₂).

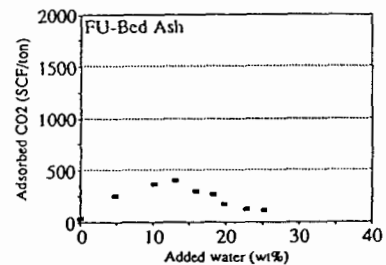
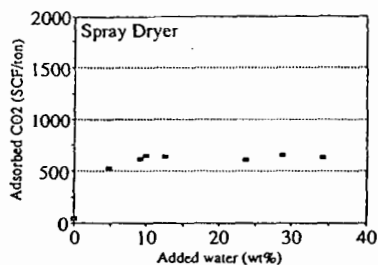
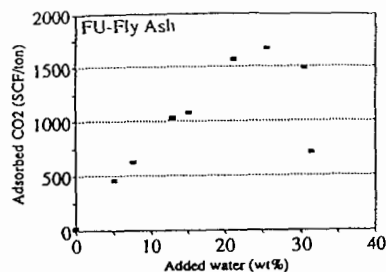
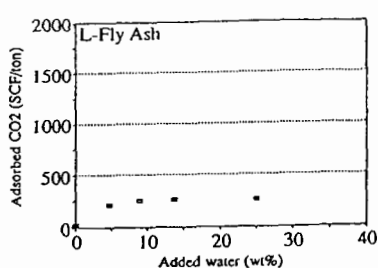


Figure 4. Absorption of CO₂ by hydrated wastes as a function of water content.

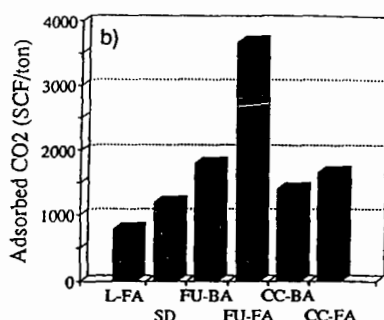
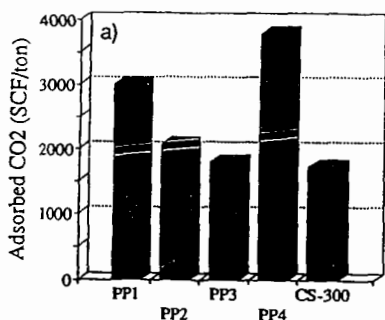


Figure 5. CO₂ absorption by water/waste slurries. a) Coolside wastes; b) all others.